Low-temperature plasma nitriding of martensitic stainless steel

K. Ram Mohan Rao[1] · **Corinne Nouveau**[2] · **K. Trinadh**[1]

Abstract This study presents the plasma nitriding of Cr–Mo–V tool steel to protect it from environmental degradation. The steel samples after metallographic polishing were nitrided in the glow discharge plasma of N_2 and H_2 gas mixture (80:20). Nitriding was performed at two different temperatures, a lower temperature of 450 °C and the higher temperature of 500 °C. The potentiodynamic polarization tests in 3.5% NaCl electrolyte had shown the enhancement of corrosion resistance of steels after nitriding. X-ray diffraction (XRD) studies and scanning electron microscopic analysis coupled with energy dispersive spectroscopic analysis (SEM/EDS) was performed to understand the modification of surface microstructure. XRD analysis of the nitrided steels revealed the presence of γ′- and ε-nitrides of iron, which were responsible for the improvement of corrosion resistance.

Keywords Corrosion · Plasma · Nitriding · Polarization · Nitrides

✉ K. Ram Mohan Rao
rammohanrao.k@gmail.com

[1] Department of Chemistry, GITAM Institute of Science, Gandhi Institute of Technology and Management, Rushikonda, Visakhapatnam, Andhra Pradesh 530045, India

[2] Laboratoire Bourguignon des Matériaux et Procédés (LaboMaP), Arts et Métiers Paris Tech de Cluny, Rue Porte de Paris, 71250 Cluny, France

1 Introduction

Chromium–molybdenum–vanadium-based tool steels used for wood machining have shown to possess good mechanical properties. However, the wear and corrosion resistance of these steels need to improve for the widespread applications. The tool industries demand the enhancement of these properties to prolong the life of tools. Hard and corrosion resistant coating, e.g. by following physical or chemical vapour deposition, on the surface of the steel can solve this problem but the poor adhesion and the delamination of the deposited layer limits its applications [1, 2]. In this regard, nitriding has already been proved to be a successful method to improve these properties without the problem of delamination of the deposited layers [3, 4]. Conventional ammonia nitriding has problems related to controllability of process parameters and side effects to the environment. Later, plasma nitriding, a versatile eco friendly, economical and more efficient method with good controllability of the process parameters has been recognized. A host of literature supports the enhancement of mechanical and corrosion resistance properties of various steels, Ti/Ti alloys, etc., by following plasma nitriding [5–31]. Plasma nitriding is vacuum-based process, involves the acceleration of nitrogen ions from its plasma source and at the desirable temperatures, heat the substrate. Nitrogen diffuses into the substrate whereupon it forms the nitrides of the substrate material and the solid solution. The details of the nitriding reactor have been presented elsewhere [12, 29].

Plasma nitriding of various steels have been reported earlier. However, so far, less is known about the nitriding effects on corrosion resistance of chromium–molybdenum–vanadium steel. Corinne et al. [5] reported the enhancement of hardness of this steel after plasma nitriding. Later,

Rao et al. [6, 9–12] worked on this steel for the enhancement of corrosion resistance. Still several aspects of plasma nitriding and its effects on this steel remain unfold. The present study focuses on the effects of low- and high-temperature plasma nitriding and its effects on corrosion resistance properties.

2 Materials and Methods

Martensitic steel samples of dimension 10 × 6 × 3 mm^3 were cut from the big sheet after hardening and tempering heat treatment. The composition of the Cr–Mo–V steel is given in wt.% as follows: Mn (0.5%), Cr (0.8%), Mo (1.5%), V(0.5%), Si (1.0%), C (0.5%) and Fe (88%).

Steel samples were kept on the sample holder inside the nitriding chamber after metallographic polishing and cleaning ultrasonically in acetone and evacuated to approx. 0.5 Pa. The samples were biased negatively at − 250 V. Initially, the Ar plasma was triggered and then Ar + ions from the plasma was bombarded on the surface and sputtering cleaned the native oxide and dirt. Ar + ion bombardment continued until the desired level of temperature was attained. Then a gas mixture of nitrogen and hydrogen at a ratio of 80:20 was filled into the chamber and it triggered the plasma. Nitrogen and hydrogen ions from the plasma accelerated towards the surface of the sample and thus initiated the nitriding cycle. Nitriding was performed at two different temperatures of 450 and 500 °C for a fixed duration of 10 h.

X-ray diffraction (XRD) and scanning electron microscopic analysis (SEM/EDS) were carried out to understand the phase formation after nitriding. To know about the corrosion resistance of all the steel samples, potentiodynamic polarization tests were performed in 3.5% NaCl electrolyte.

3 Results and Discussion

3.1 Phase Evolution Following XRD

Nitrided steels after XRD studies have shown the presence of Fe-nitrides (Fig. 1). Figure 1a represents the XRD pattern of bare steel showing only the Fe peaks and these are Fe (110), Fe (200) and Fe (211). Figure 1b, c represent the XRD patterns of nitrided steels at 450 and 500 °C, respectively. Both of these steels have shown the presence of lower nitrides γ' (Fe_4N) and also the ε ($Fe_{2-3}N$)-nitride peaks. These nitrides are available in the nitrided layer and are known to improve the hardness and corrosion resistance of the steel. Rao et al. [6] have shown a significant improvement of hardness to around 1200 H_v from its initial hardness of around 650 ± 30 H_v, after nitriding for 6 h at 450 °C. Fe (100) the major iron peak seems to be shifted slightly towards the left of its initial position, which may be due to the nitrogen supersaturation and formation of expanded martensite. The presence of γ' (Fe_4N) and also the ε ($Fe_{2-3}N$) and nitrogen super saturation is responsible for the improvement of hardness as stated earlier [5, 6]. Figure 1 shows that the concentration of iron nitrides after nitriding at 500 °C is more than that shown after nitriding at 450 °C. Hence, the resistance to corrosion is expected to be more after nitriding at higher temperature.

3.2 Scanning Electron Microscopic (SEM) Analyses

Cross-sections of the nitrided steels were mirror polished and etched with Villela's reagent. SEM/EDS of cross-sections of steels nitrided at 450 and 500 °C for 10 h have been presented in Fig. 2. Obviously, the thin uniform layer at the surface also called as compound layer is good from the wear resistance point of view. A thick layer may not be good for wear resistance of the nitrided steel. Thus, a thin layer known to be corrosion resistant layer will be responsible for the enhancement of corrosion resistance of the nitrided steel. Compound layer is followed by diffusion layer enriched with γ'- and ε-nitrides augment the resistance to corrosion. EDS point analysis is performed at different points from the surface towards the bulk. The elemental point analysis at the surface level for the steel nitrided for both lower and higher temperatures are presented in Fig. 2. EDS analysis confirm the presence of nitrogen in the nitrided steel. At 500 °C, the concentration of nitrogen is found to be almost same as that for the steel nitrided at 450 °C. This may be atttributed to the faster diffusion of nitrogen and hence its retention on the surface level decreases to a level equivalent to that of the steel nitrided at lower temperature (Fig. 3).

3.3 Electrochemical Characterization

Corrosion resistance was assessed by following potentiodynamic polarization tests in 3.5 wt.% NaCl. For the polarization tests, the potentiostat (Model SI1287 Electrochemical 26 Interface-Solatron-Analytical, made in UK) was used. The corrosion cell consists of the nitrided steel as working electrode, a reference electrode [saturated calomel electrode (SCE)] and the Pt counter electrode in 3.5% NaCl.

Steel samples were first immersed in a 3.5% NaCl solution and after attaining the stable potential, potentiodynamic polarization tests were performed. After 3000 s, equilibrium potential was set to ∼ − 0.50 V for bare steel and for the nitrided steel ∼ 0.49 V, i.e. almost equally resistant to corrosion.

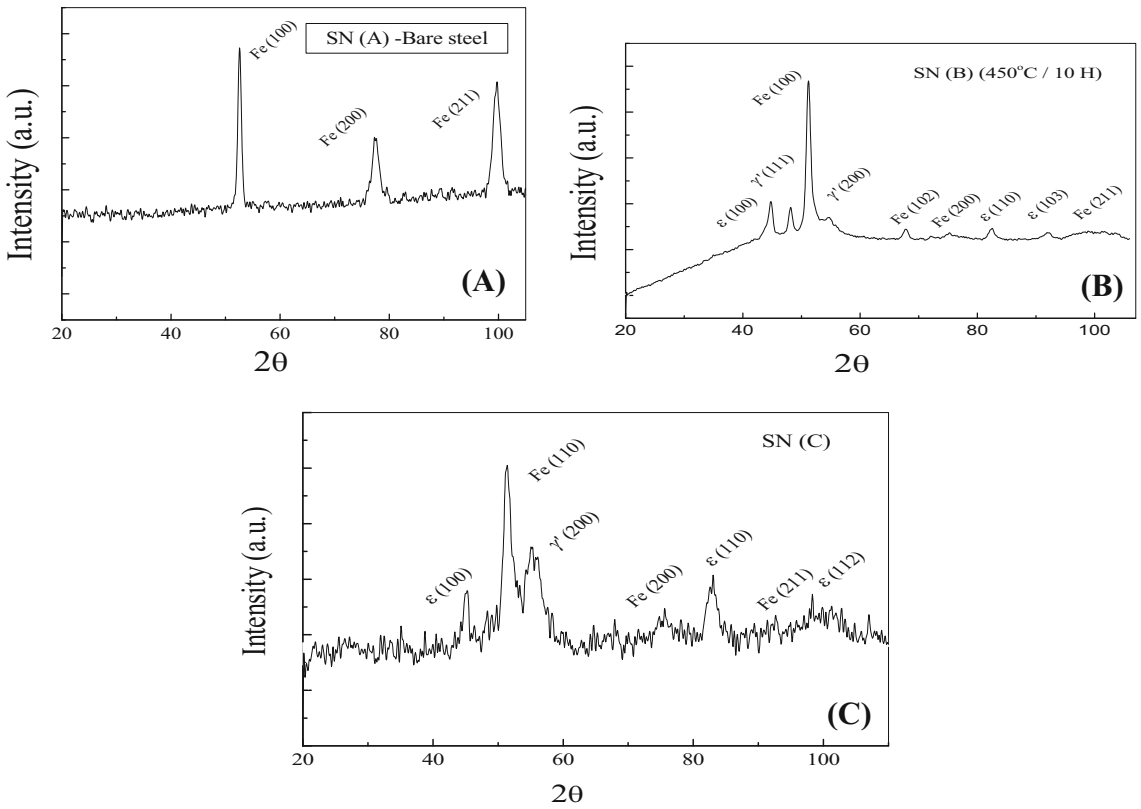

Fig. 1 XRD patterns of → bare steel SN(A); the steel nitrided for 10 h at 450 °C (SN(B)) and SN(C) 500 °C

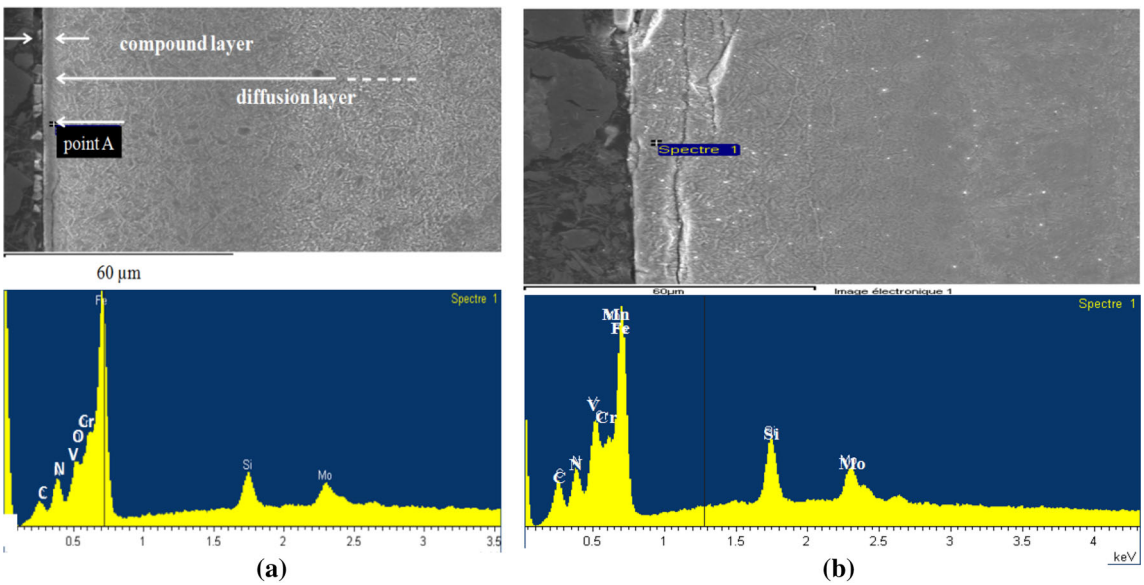

Fig. 2 SEM micrograph coupled with EDS for steel after nitriding at **a** 450 °C and **b** 500 °C for the duration of 10 h (× 1000; etched with the Villela's reagent)

It is evidenced from the above polarization diagrams that the steel nitrided at 450 °C for 10 h has shown more propensities to corrosion when compared to the bare steel. However, a wider range of corrosion resistance like passivation, has been shown by the nitrided steel. The steel nitrided at higher temperature has shown more positive potential than that of nitrided steel at lower temperature. This reflects that the steel nitrided at higher potential has less propensities towards corrosion than the steel nitrided at

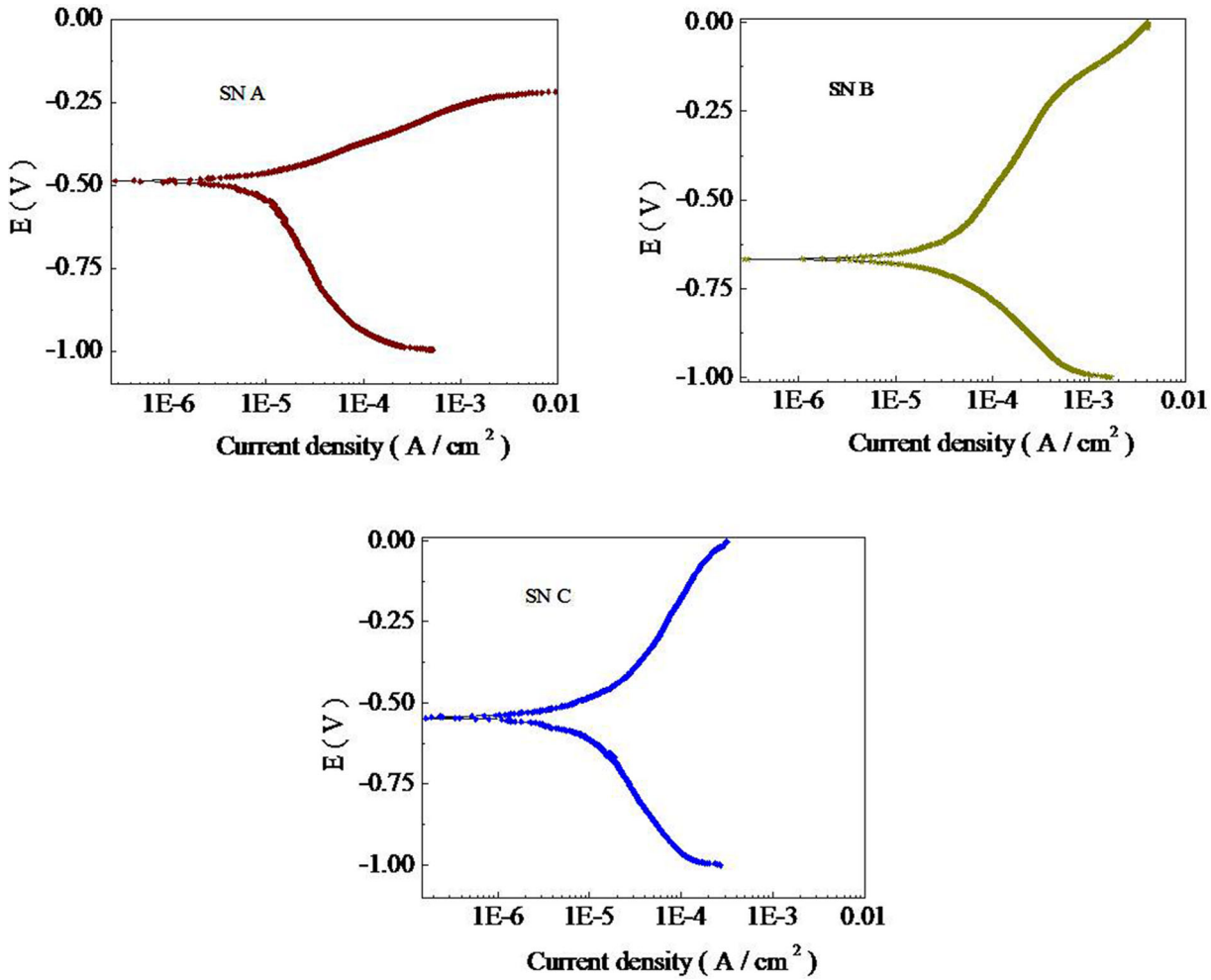

Fig. 3 Electrochemical potentiodynamic polarization curves of → SN(A) bare steel and the nitrided steels SN(B) (at 450 °C) and SN(C) (500 °C) in NaCl (3.5 wt.% NaCl)

Table 1 Corrosion parameters calculated from Tafel's extrapolation after potentiodynamic polarization of bare and nitrided Cr–Mo–V steel in 3.5% NaCl

Sample code	Corrosion rate (MPY)	I_{corr} (Amp/cm^2)	E_{corr} (V) SCE
SN(A)	3.6597	8.6779E−6	− 0.49579
SN(B)	7.6602	1.8164E−5	− 0.66333
SN(C)	1.6153	3.8302E−6	− 0.54563

lower potential. From Tafel's extrapolation, the corrosion parameters have been calculated (Table 1).

The dissolution kinetics of the nitrided steel at higher temperature is slower as compared to that of the bare steel. I_{corr} value 8.6779E−6 Amp cm^2 for the bare steel is more than 3.8302E−6 Amp cm^2 as shown by steel SN(C). Steel SN (B) has shown the highest value of I_{corr}, which is around 1.8164E−5 Amp cm^2. This may be due to the surface heterogeneity or the delayed passivation. The corrosion rate as shown by the SN(C) has been found to be the lowest 1.6153 MPY. From XRD, it is evidenced that the nitride concentration and specifically the ε-nitride is more in SN(C) than that shown by SN(B). It is known already that the ε-nitride has good corrosion resistance property. Moreover, the wider range of corrosion resistance as passivation layer is shown by the nitrided steel which may be due to the release of nitrogen from the solid solution. The released nitrogen increases the alkalinity of the electrolyte. The alkalinity does not favour the corrosion, thus synergistically augmenting the resistance to corrosion along with the resistance shown by iron nitrides. It was found previously [5, 6] that the plasma nitriding of similar steel at a

lower temperature of 450 °C significantly improves the hardness; the present study shows the improvement of passivation region or the corrosion resistance. Also true for the steel SN(C) that the hardness improves after plasma nitriding at a higher temperature of 500 °C for 10 h and the present study has shown the significant improvement of corrosion resistance. Results derived from the previous studies show that the plasma nitriding at both lower as well as higher temperature is useful for the enhancement of hardness [5, 6] and corrosion resistance. However, the best suggested condition for the improvement of corrosion resistance is nitriding at the higher temperature of 500 °C.

4 Conclusions

From the present study, it is concluded that the plasma nitriding in the plasma of N_2 and H_2 gas mixture at the ratio of 80:20 successfully improves the corrosion resistance of tool steel. In the environment where Cl^- is the common corrodent, the tool life can be prolonged after nitriding and thus save the replacement cost. The observed increase of corrosion resistance may be attributed to the presence of iron nitrides Fe_xN (x = 2–3, 4) as well as the nitrogen present in the solid solution. Previous study [6] has shown that the hardness has improved after nitriding at low temperature. However the present study shows that a wider region called as passivation zone is the added advantage. Moreover, nitriding at 500 °C for the given time of 10 h has shown better condition for the enhancement of corrosion resistance. Thus, for this tool, steel plasma nitriding enhances the corrosion resistance and thus beneficial for its widespread application.

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